Fundamental Reactivity Testing and Analysis of Hydrogen Storage Materials & Systems

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SAVANNAH RIVER NATIONAL LABORATORY
We Put Science To Work

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Savannah River National Laboratory

Project ID #: ST 40

Overview

Timeline

- Start: 10/1/05
- End: 9/30/10
- Percent complete: 30%

Budget

- Proposed Budget: $2M
- Funding received in FY07
  - $300K
- Funding for FY08
  - $500K

Barriers Addressed

- D. Durability/Operability
- A. System Weight and Volume
- Q. Reproducibility of Performance
- F. Codes and Standards

Partners

- **M. Fichtner,** Forschungszentrum Karlsruhe, Germany
- **N. Kuriyama,** National Institute for Advanced Industrial Science and Technology, Japan
- **R. Chahine,** Université du Québec à Trois-Rivières, Canada
- **D. Mosher,** United Tech. Res. Ctr., USA
- **D. Dedrick,** Sandia NL, USA

DoE On-Board Hydrogen Storage Technical Targets

Target	2007	2010	2015
Wt % H_2 (Useable)	4.5	6	9
Vol. Cap. (kg H_2/L)	0.036	0.045	.081
Cycles	500	1000	1500
Minimum rate (g/s)/kW	.02	.02	.02
Minimum/Maximum pressure (atm) [FC]	8/100	4/100	3/100
Minimum/Maximum ambient temperature (°C)	-20/50	-30/50	-40/60
Start time to full flow (s)	4	4	0.5
System fill time (min)	10	3	2.5
Safety	Meet or exceed applicable standards		

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Task Plan

- *Task 1: Risk Assessment*
  - Assess the potential risks of using solid state hydrides
  - Develop test protocols and experimental designs to aid in characterization of hypothetical accident scenarios
  - Test six compounds in three discharge states using standardized semi-quantitative test methods
- *Task 2: Thermodynamics & Chemical Kinetics*
  - Quantitatively assess chemical reactions of compounds with air, water & other engineering materials
- *Task 3: Risk Mitigation*
  - Quantitatively assess chemical reactions of compounds with potential inhibitors
  - Evaluate efficacy of inhibitors in laboratory scale tests
- *Task 4: Prototype System Testing*
  - Design assemble and test prototype storage systems to evaluate effectiveness of inhibitor systems.

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Materials Test Plan

- All three major classes of condensed hydrogen storage materials are being studied: metal hydrides, chemical hydrides & adsorption hydrides.
- Priority of analysis is being conducted in consultation with the three Materials CoE's and DoE.

Little Known

Investigations Initiated

1. *$2LiBH_4 + MgH_2$*
2. *NH_3BH_3*
3. Activated Carbon
4. AlH_3

Some Known

Complete Analysis

- $NaAlH_4 + 2\%TiCl_3$
- $2LiH + Mg(NH_2)_2$
- Mg_2NiH_4
- $LaNi_5H_6$

Materials Prep Plan

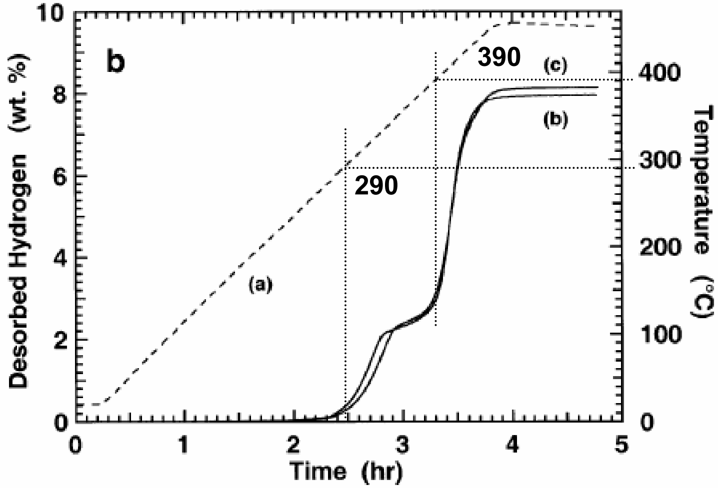
- Use Particle Size
  - Fully Charged
  - Partially Discharged
  - Fully Discharged

Background: $2LiBH_4$+MgH_2

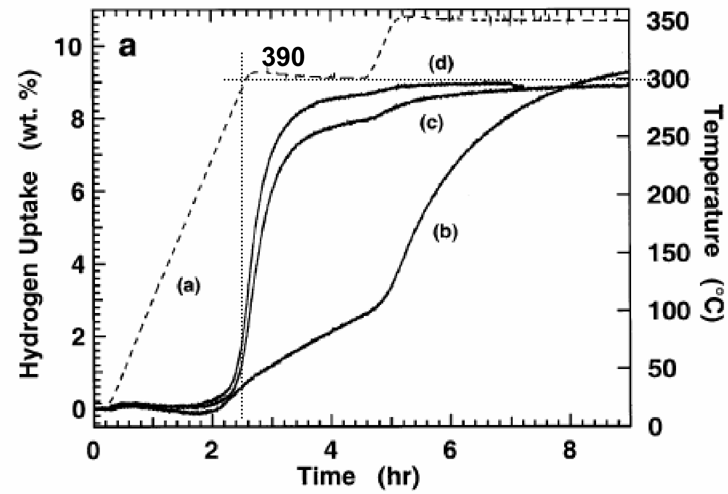
$$2LiBH_4 + MgH_2 + 3m\%TiCl_3 \Rightarrow 2LiH + MgB_2 + 2H_2$$

J. Vajo, J. P. Chem. B Letters, Vol 109, pg 3719 (2005).
wt% = 11.4%
ΔH = 40.5 kJ/mole H_2

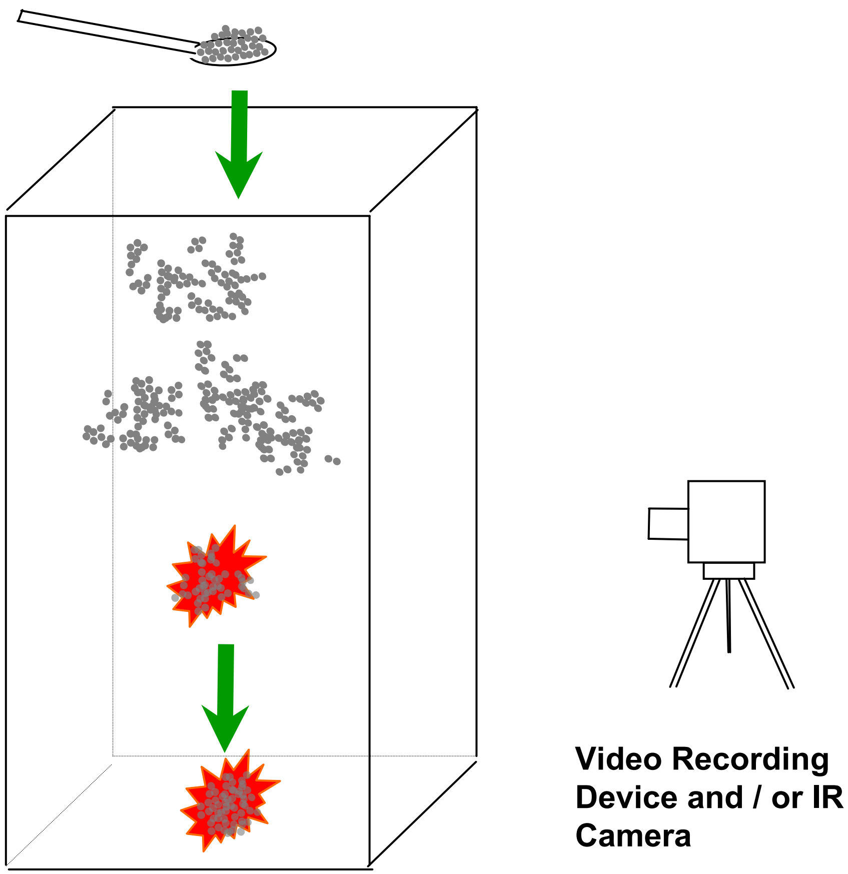
discharge



Recharge: 100 bar



Apparatus for Pyrophoricity Test



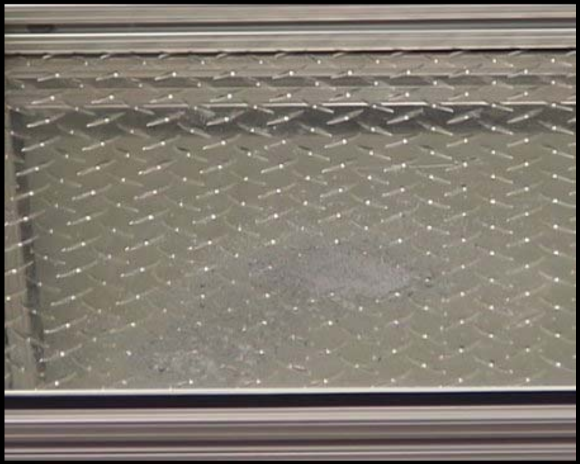
1. Drop a small amount (< 1 g) of material in a containment box under ambient conditions
2. Observe material as it falls and for a period of < 5 min. after falling.
3. Check for:
   1. Gas evolution
   2. Spontaneous ignition
4. Video record experiment

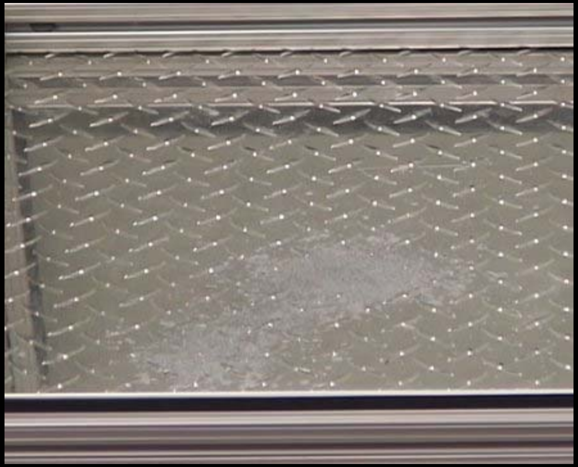
$2LiBH_4$+MgH_2 Pyrophoricity Test

Materials do not undergo reaction in air

time

Hygroscopic material absorbs H_2O from air



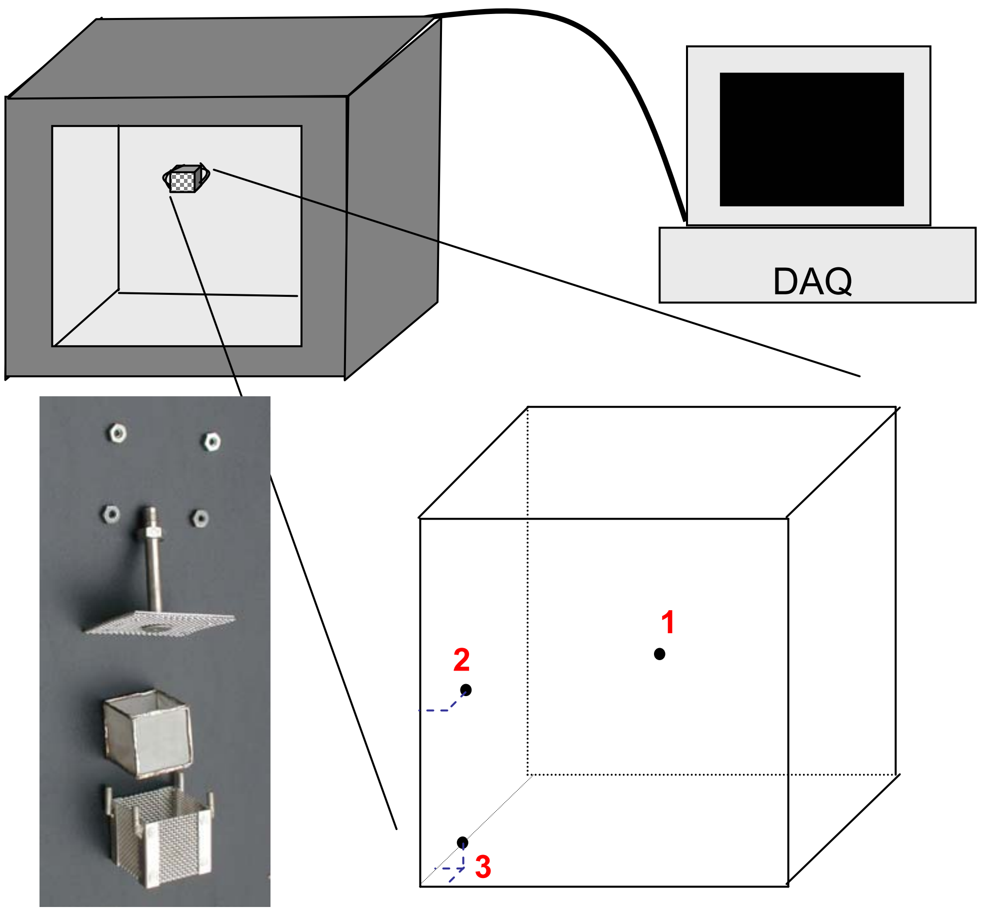


No reaction in 15 minutes (5 minutes for standard test)

time

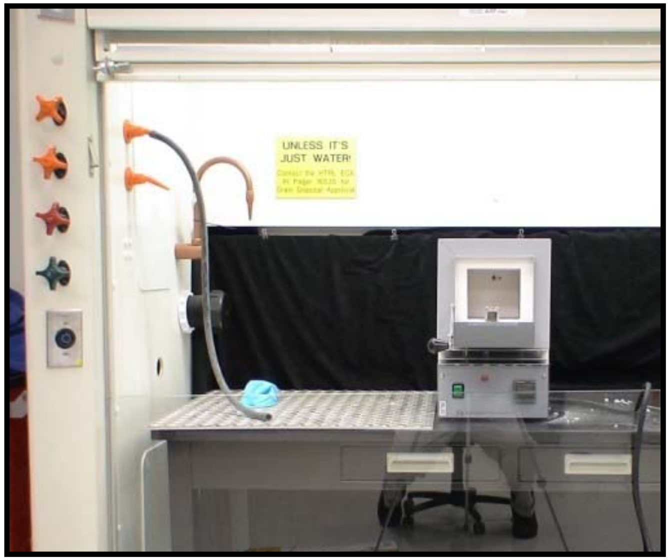
2LiBH4+MgH2 not pyrophoric

Instrumented Apparatus for Self-Heating



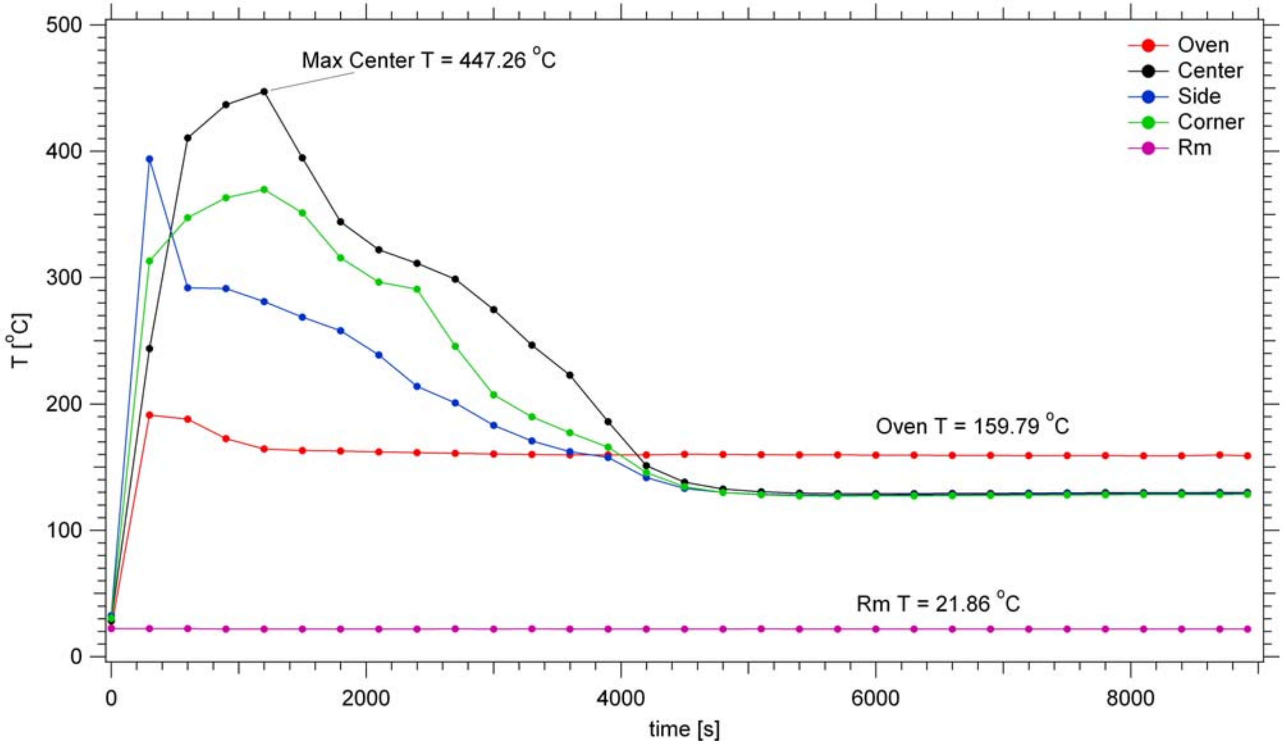
(25 mm)^3 wire mesh sample basket

- Fill the 25mm^3 sample holder with material
- Sample holder pre-fitted with micro thermocouples
- Heat sample to 150^{o}C
- Observe temperature within sample spatially resolved to determine if self-heating occurs



$2LiBH_4+MgH_2$ Self-Heating

- **Sample begins to self-heat within 30 seconds of exposure in the oven**
- **Maximum Temperature observed = 447°C**



- Reaction initiates at sample surfaces and propagates towards the interior
- Consistent with diffusion of air/water vapor into the packed powder sample

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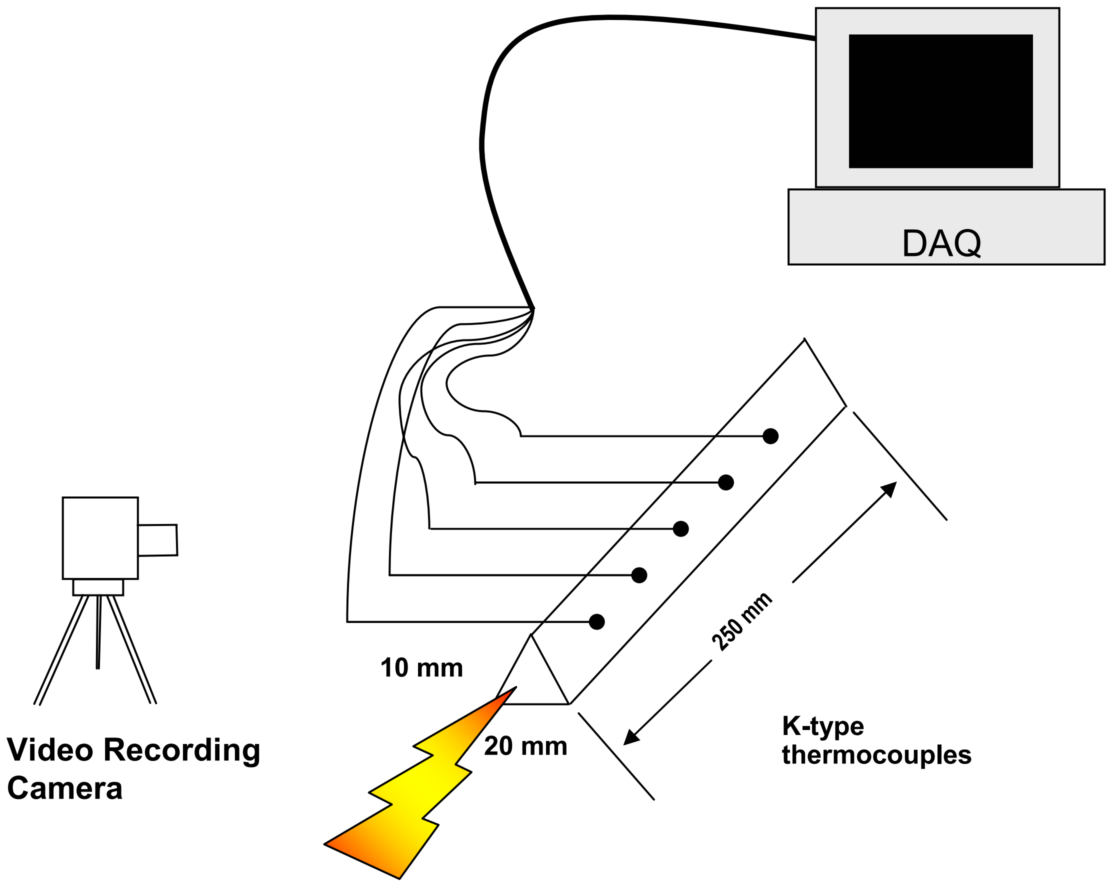
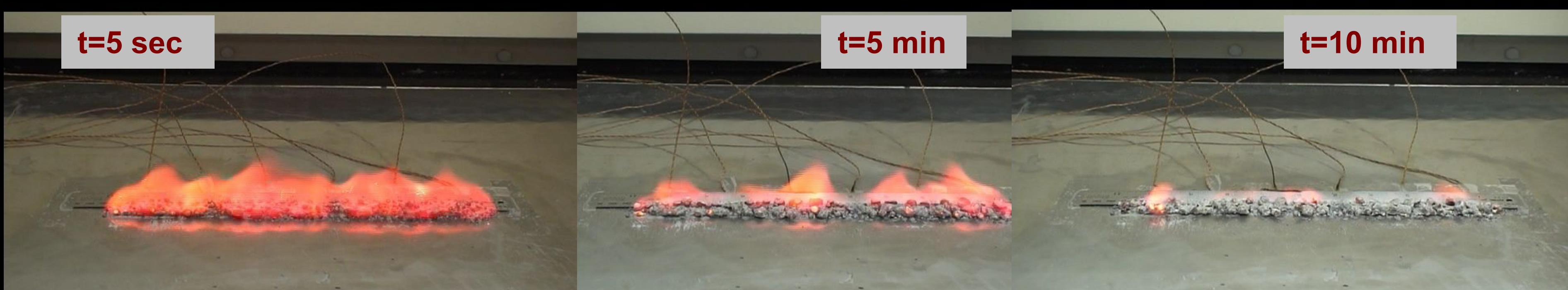
Apparatus for Burn Rate Test



1. Pack a triangular prism mold 20mm x 10mm x 250mm with material
2. Place material on fire resistant base, with thermocouples fitted underneath at 35mm intervals
3. Introduce flame at one end of packed material
4. Observe whether flame propagation occurs
   1. Measure rate of propagation
   2. Monitor linear temperature distribution

$2LiBH_4+MgH_2$ Burn Rate

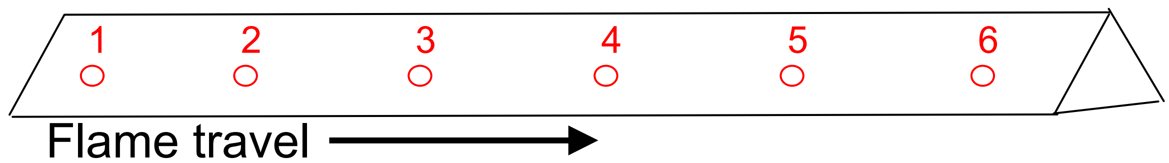
time

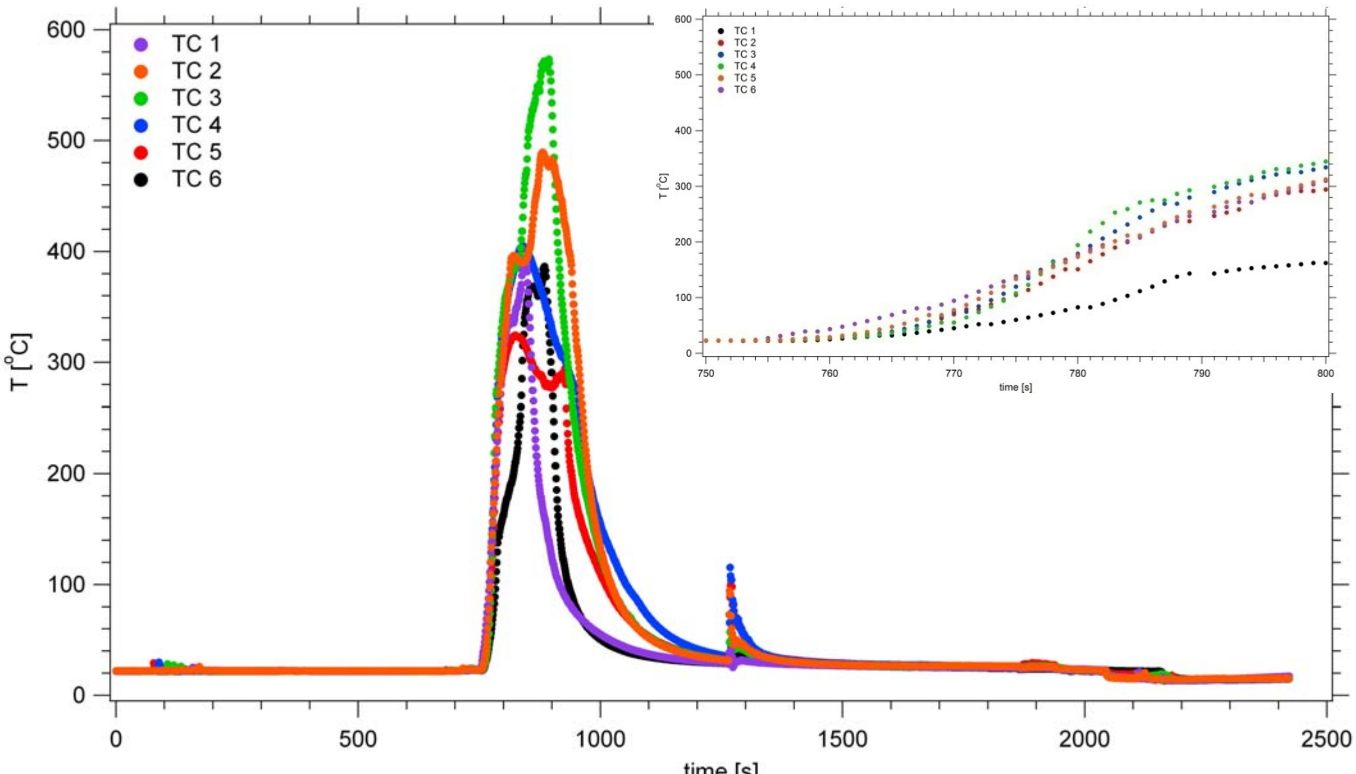


Flame rapidly moves to right and continues to burn for several minutes

time

$2LiBH_4 \cdot MgH_2$ Burn Rate Measurement





- **Burn rate**
  = 52 mm/sec
- **Burn rate for $NaAlH_4$**
  = 51 mm/sec[1]

- Variations in max temperature attributed to variations in packing density.
- Burn rate is very similar to $NaAlH_4$

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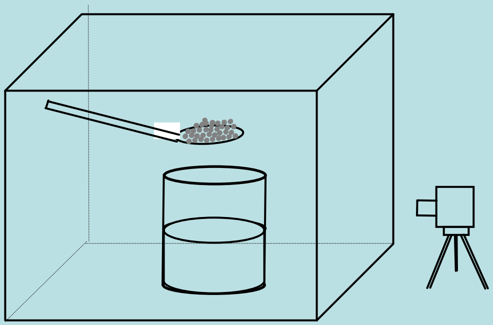
[1]Mosher *et al*, **446**, *J. Alloys and Compounds*, pp. 707 (2007)

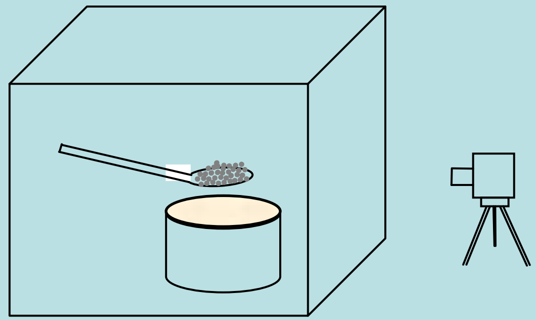
Experimental Setup of Water Contact Tests

Water Immersion



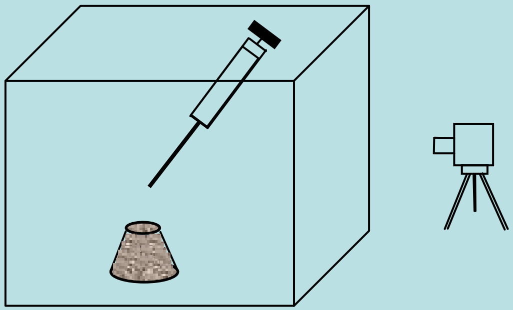
1. Drop ~ 20 mg of material into excess of H_2O (250 ml)
2. Check for:
   a) Gas evolution
   b) Spontaneous ignition
3. Video record experiment

Surface Contact



1. Drop ~ 20 mg of material onto filter paper on the surface of an excess of H_2O (250 ml)
2. Check for:
   a) Gas evolution
   b) Spontaneous ignition
3. Video record experiment

Water Drop



1. Contact a small pile (~ 2 g) of material with a few drops of H_2O
2. Check for:
   1. Gas evolution
   2. Spontaneous ignition
3. Video record experiment

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$2LiBH_4 \cdot MgH_2$ Water Immersion

t=0 sec

T = 2 sec

time

H_2 bubble evolution

t=2 min

Coalescence and sinking of products

t=7 min

time

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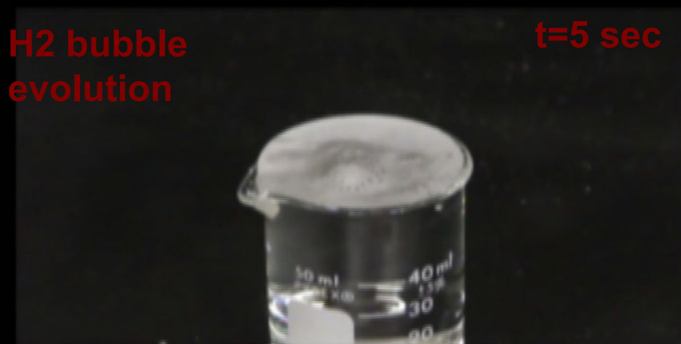
Material does not ignite on dropping in excess water

$2LiBH_4 \cdot MgH_2$ Surface Contact



time

Conflagration of hydrides and hydrogen gas

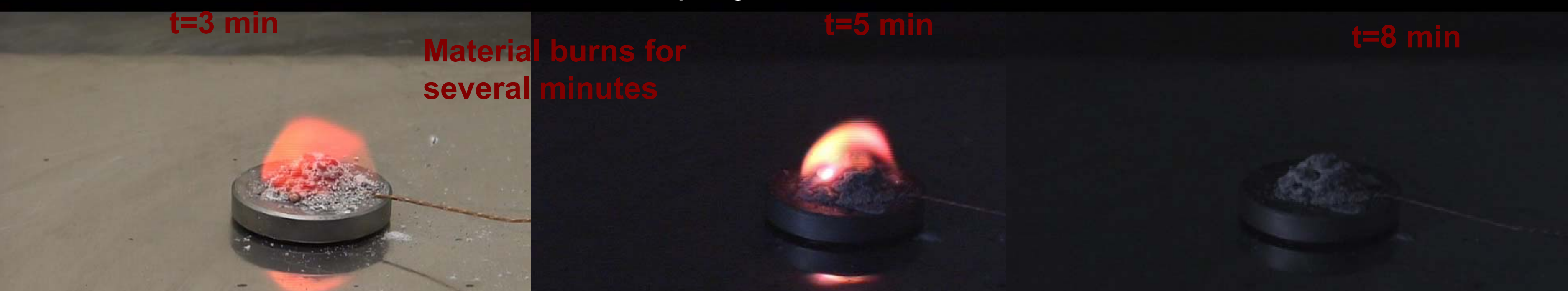
time

Material ignites on restricted contact with water and air

$2LiBH_4 \cdot MgH_2$ Water Drop

t=0 sec t=2 sec t=3 sec

time



time

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MgH_2-Hydrophobic - $LiBH_4$ -Hydrophilic
Material ignites when enough heat and hydrogen are generated

Standardized Tests for $2LiBH_4 \cdot MgH_2$

UN Test	Result	Comments
Pyrophoricity	Pass	No combustion event. Hygroscopic material absorbed H_2O from air.
Self-Heat	Fail	Self-heated ~300°C within 30 sec.
Burn Rate	Fail	Flame propagated at a burn rate of 52 mm/sec.
Water Drop	Fail	2 H_2O drops required for near-instant combustion.
Surface Contact	Fail	Restricted H_2O surface contact results in combustion
Water Immersion	Fail	No combustion event recorded. Gas evolved at longer times. (5 min)

- Material is classified as packing class 4.3 – Dangerous When Wet
- Same packing class as pure components

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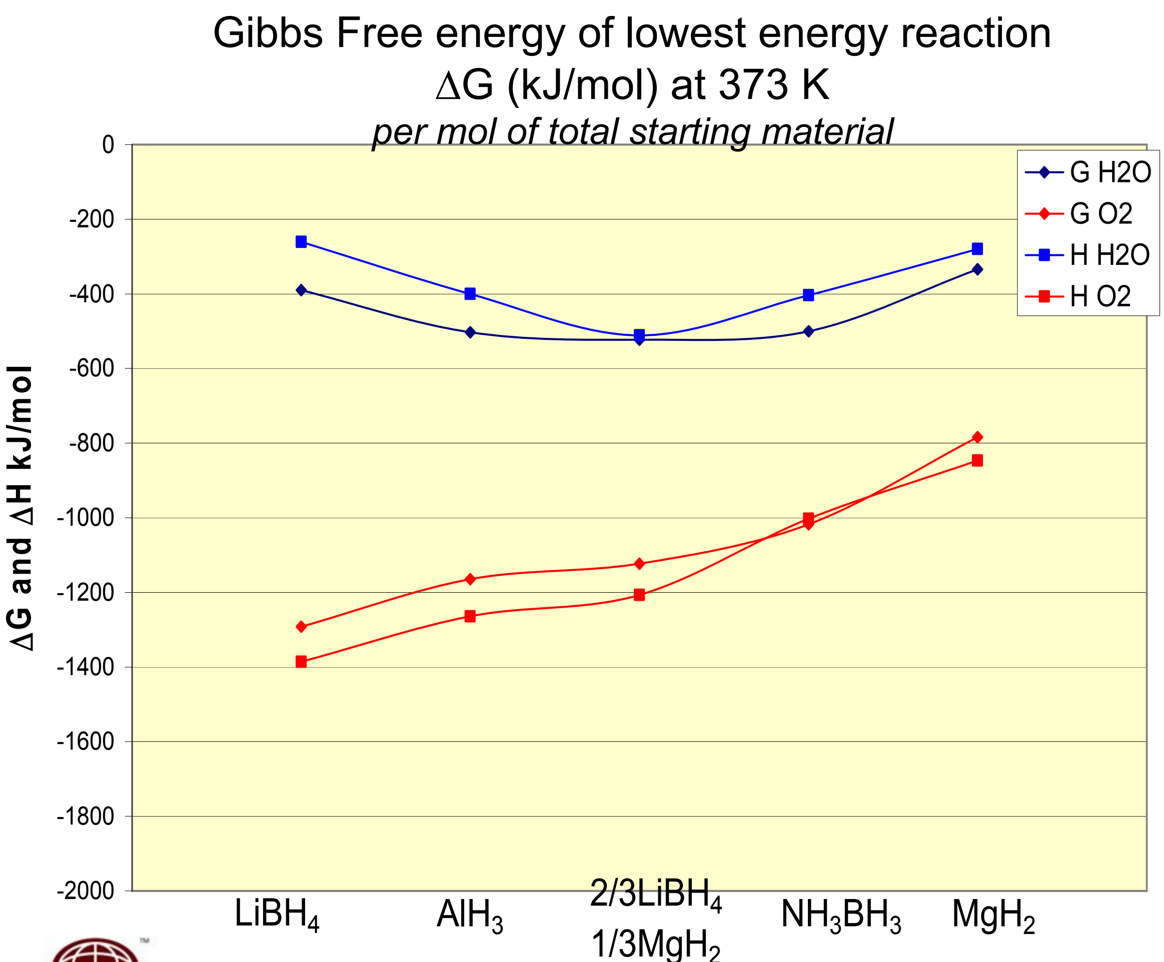
Thermodynamic Assessment of Environmental Exposure

- **Thermodynamic analysis completed for all materials available in the data base**



- Thermodynamics predict greatest energy release for oxygen reactions
- Generally, thermodynamic calculation did not predict experimentally observed products

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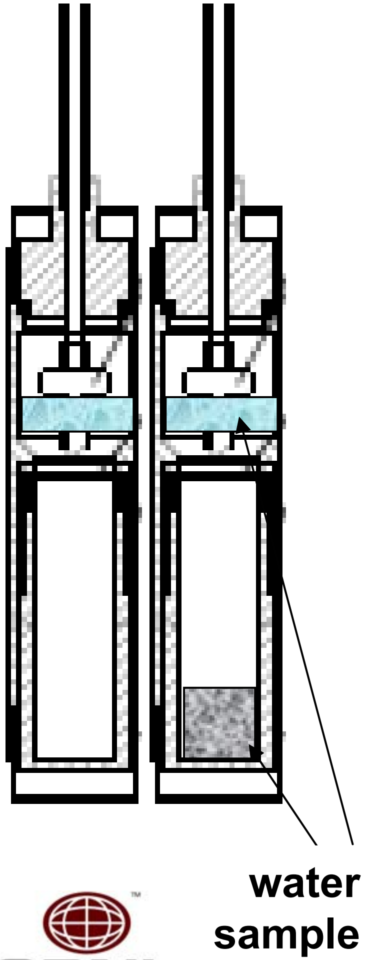
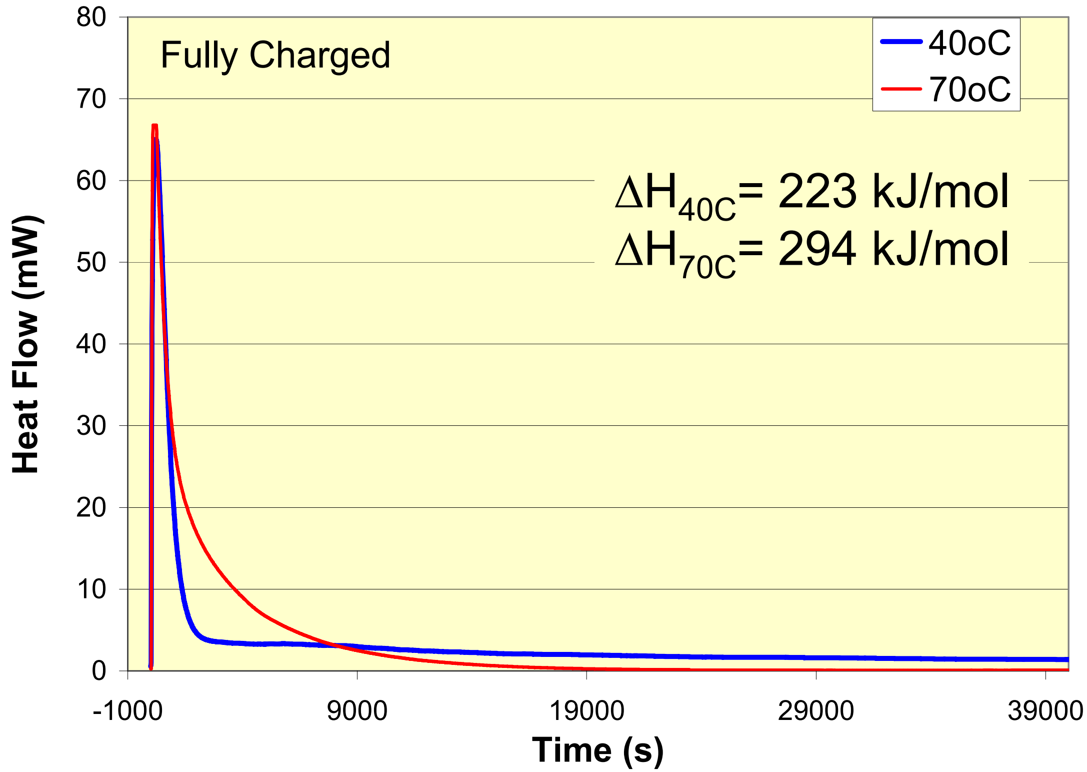
Thermo-Chemical Analysis of Water Contact

Calorimetric Apparatus



Calorimetric signal from mixing ~ 10 mg $2LiBH_4 + MgH_2$ and 1ml water at 40°C and 70°C



- More complete reaction or additional reactions occurring at 70°C.
- Investigating NMR and Raman of products to elucidate reactions.

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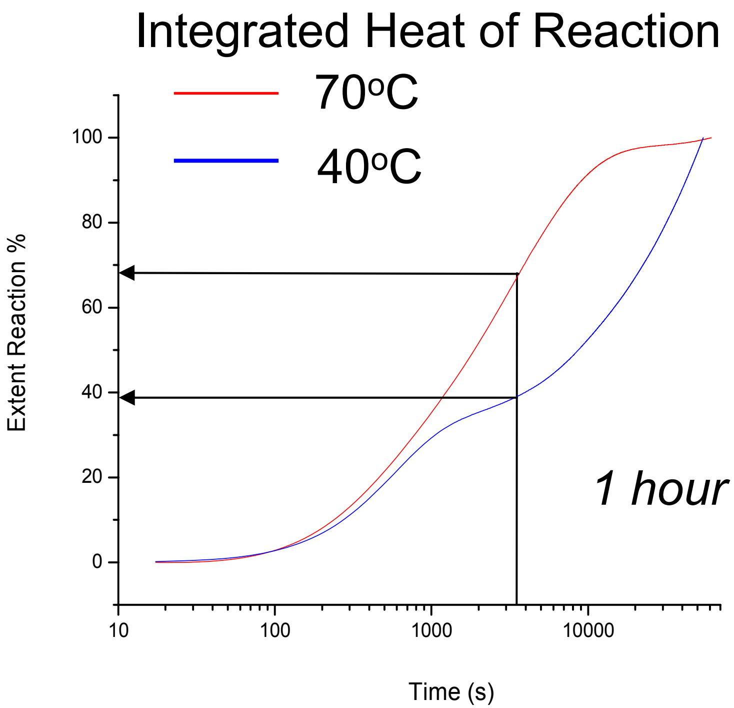
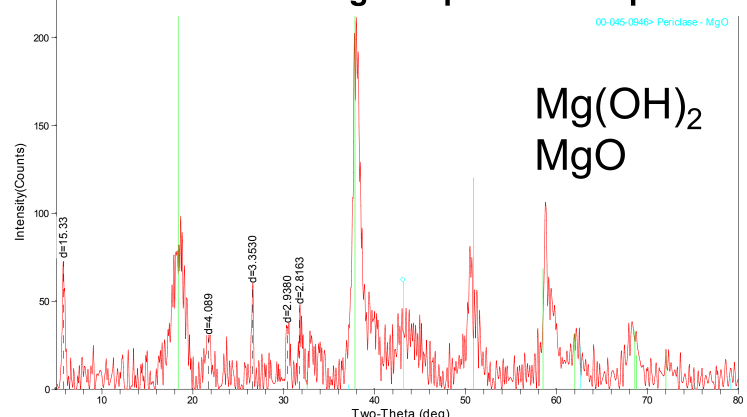
Kinetics of Water Contact: $2LiBH_4+MgH_2$

Fully Charged

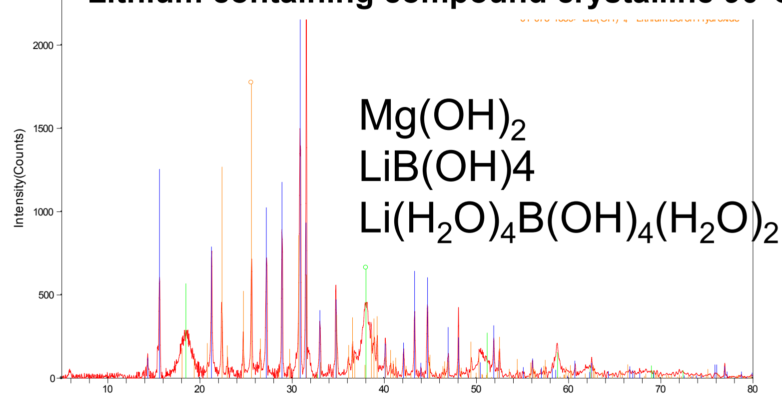


Lithium containing compound amorphous 40°C



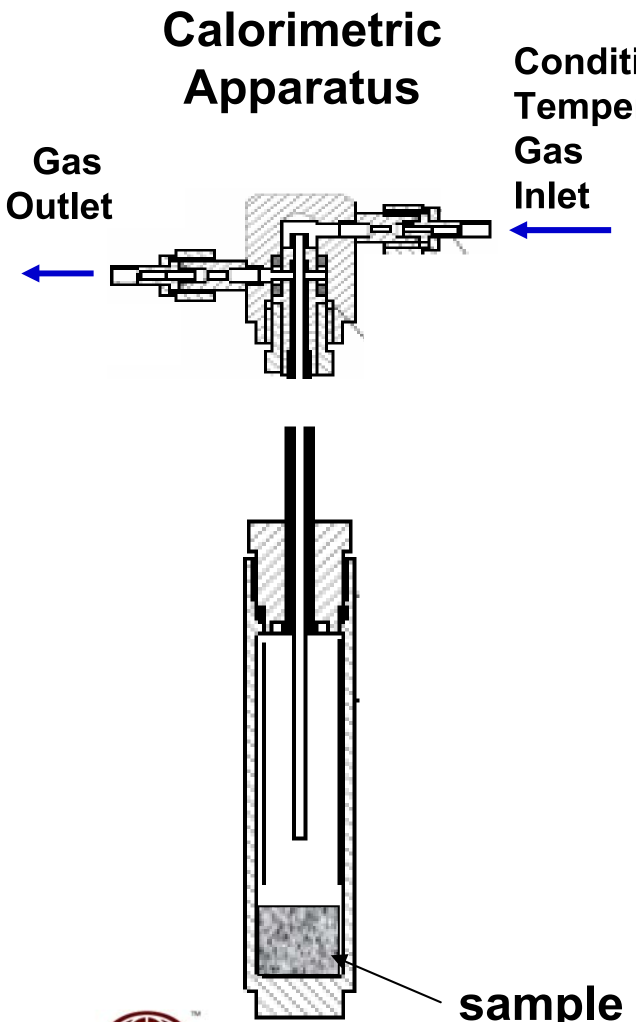
Different Products at Different Temperature

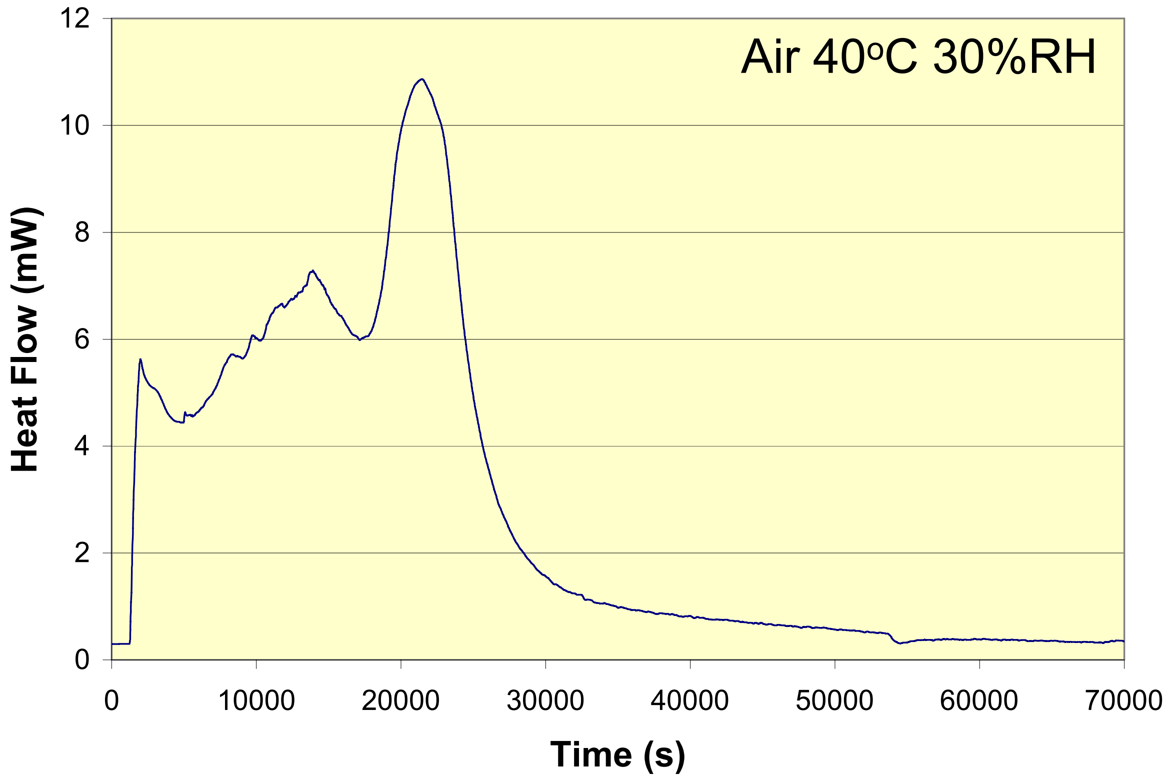
Lithium containing compound crystalline 90°C



Different reaction products is further evidence of differences in reaction pathway previously identified

Thermo-Chemical Analysis of Humid Air Exposure





Reaction profile resembles multi-step reaction or surface spallation effect, not a single step reaction.

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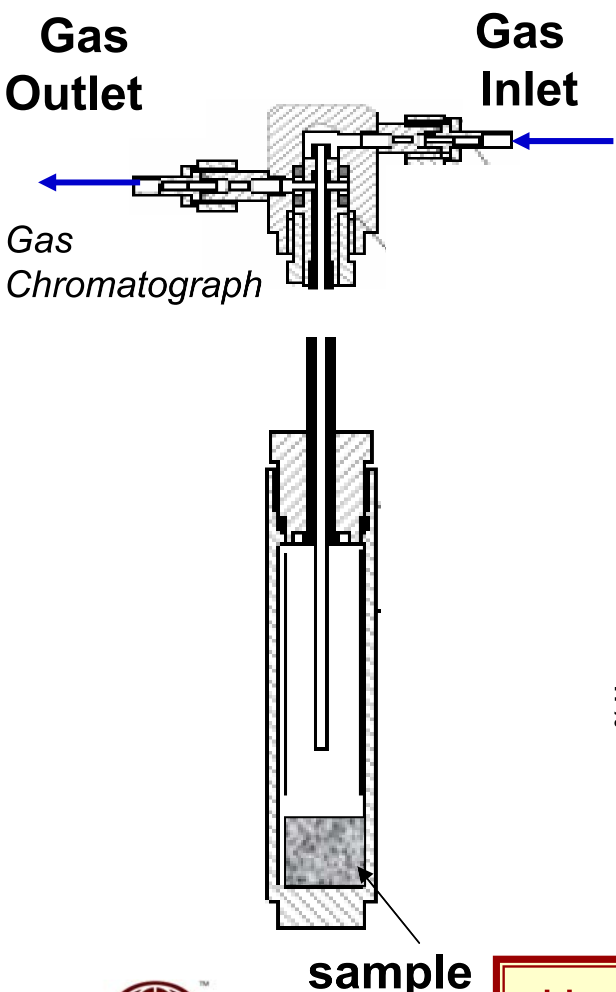
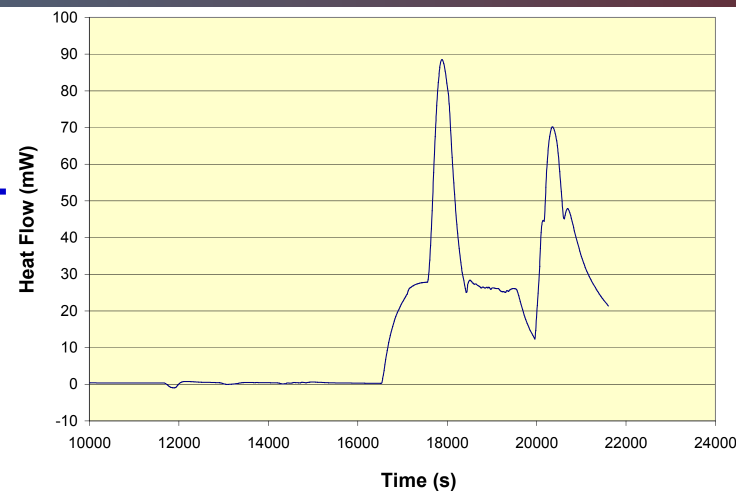
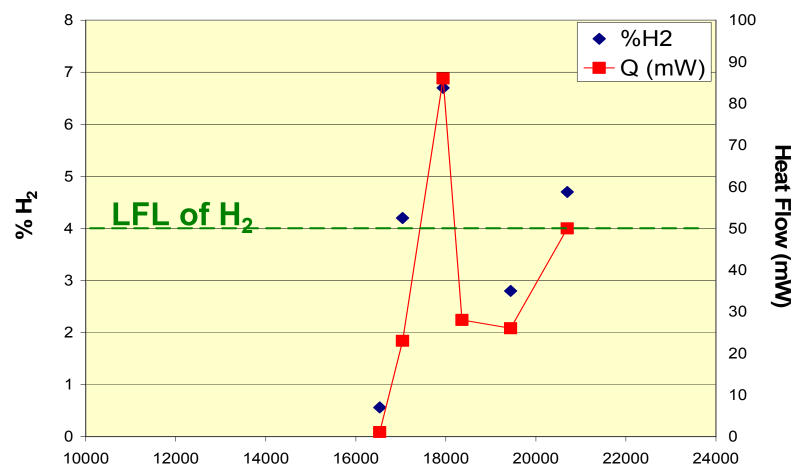
Gas Product Analysis





$2LiBH_4 + MgH_2$ calorimetry in air at 70°C and 30% RH

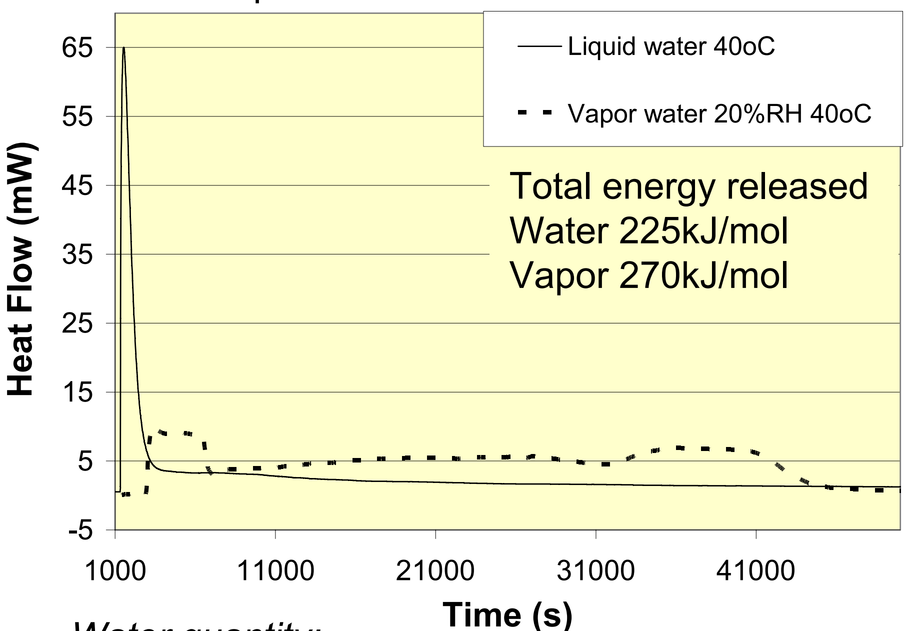


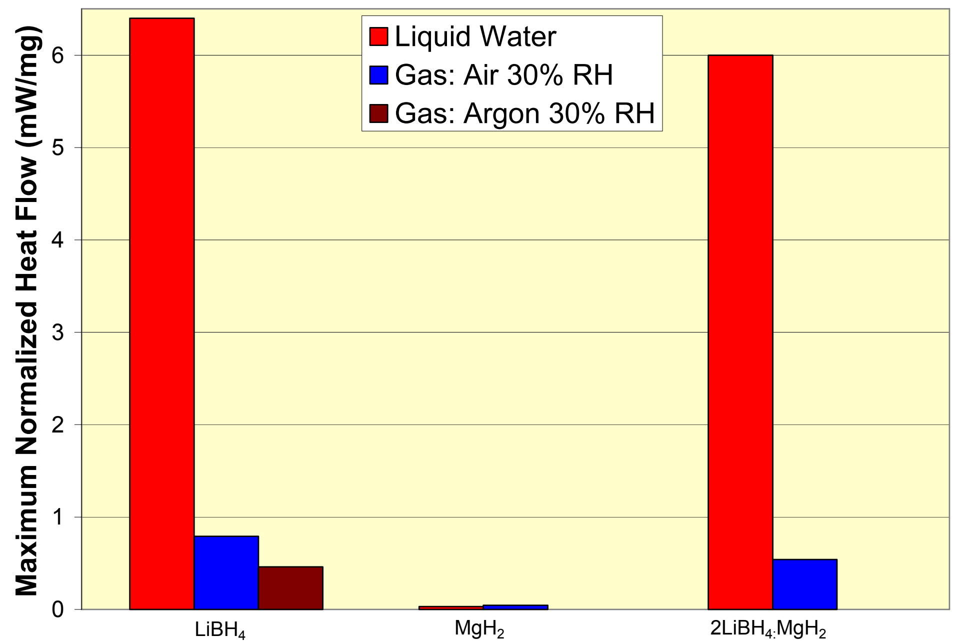
Heat flow signal during gas sampling (sample time ~ 1 min.) vs. H_2% determined via Gas Chromatography (GC)

- Hydrogen concentration in gas stream tracks heat flow signal
- Flammable concentrations of hydrogen observed

Gas versus Liquid Hydrolysis/Oxidation Comparison

Heat flow during hydrolysis with 40°C humid air 20% humidity and 40°C liquid water





Water quantity:

Liquid: t=0, mol actual/mol stoichiometric=32%

Gas: $t_{stoichiometric}$=3.5 hours t=12 hours, mol actual/mol stoichiometric=350%

- Liquid water hydrolysis displays maximum heat flow
- Oxygen in air is only a small contributor to heat flow signal

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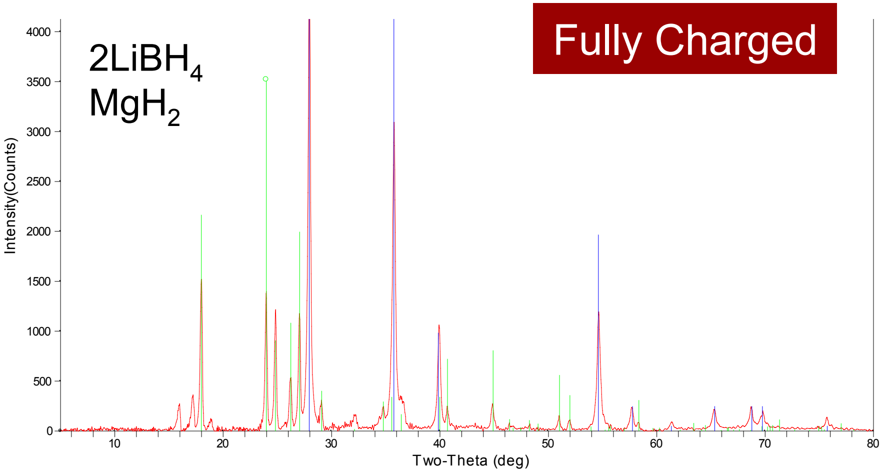
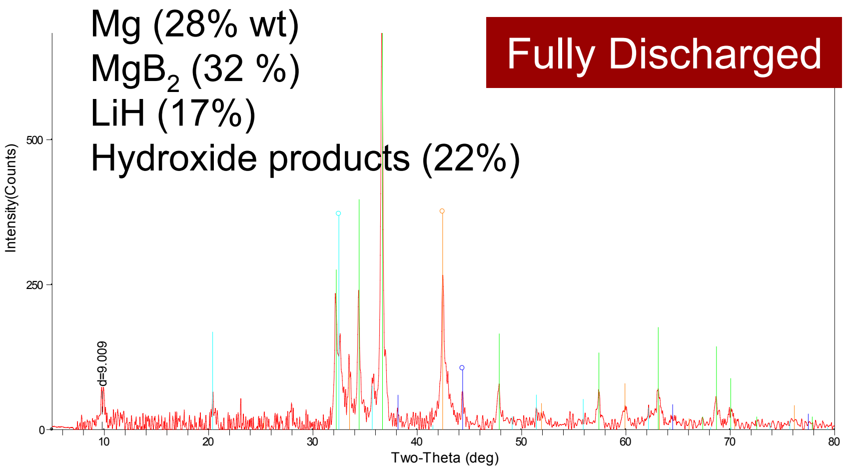
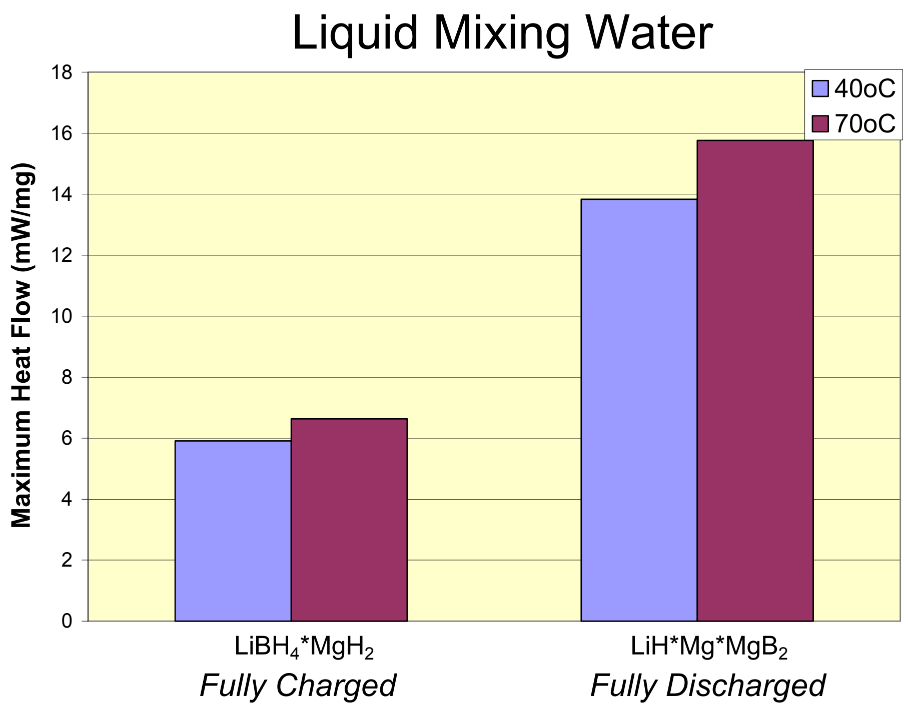
Reactivity Comparison







Discharged material state more reactive:

Charged

$LiBH_4 + 1/2MgH_2 + 4H_2O(l)=LiOH + ½\ Mg(OH)_2 + H_3BO_2 + 4H_2(g)$

ΔH= -675 kJ/ formula unit

Discharged

$LiH + 1/2\ MgB_2 + 4\ H_2O(l) = LiOH + 1/2Mg(OH)_2 + H_3BO_2 + 2H_2(g)$

ΔH= -760 kJ/formula unit

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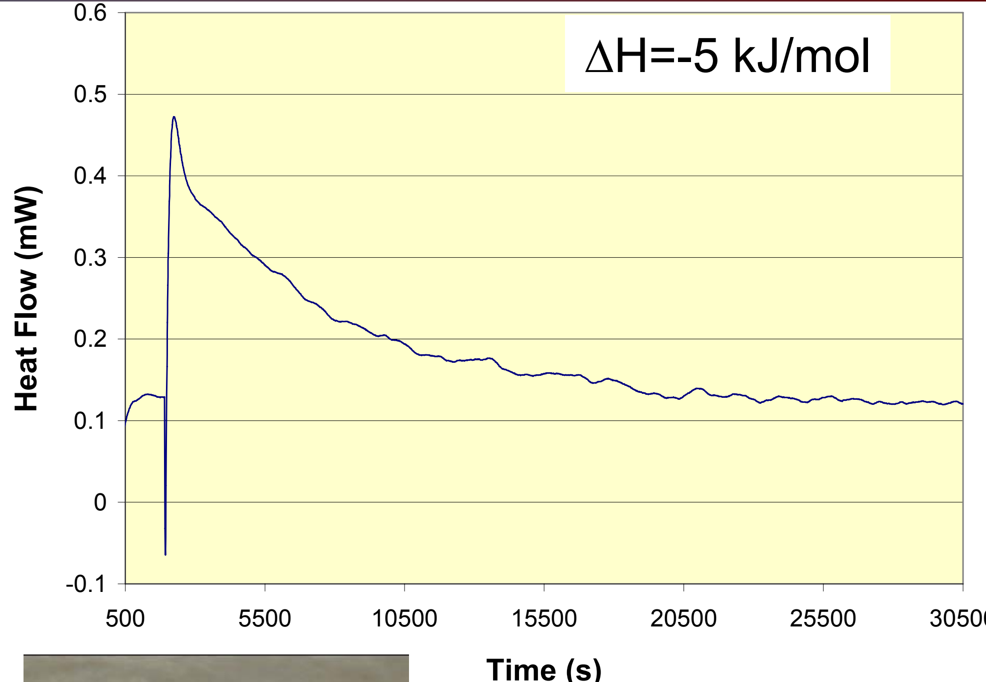
Preliminary NH_3BH_3 Testing Initiated

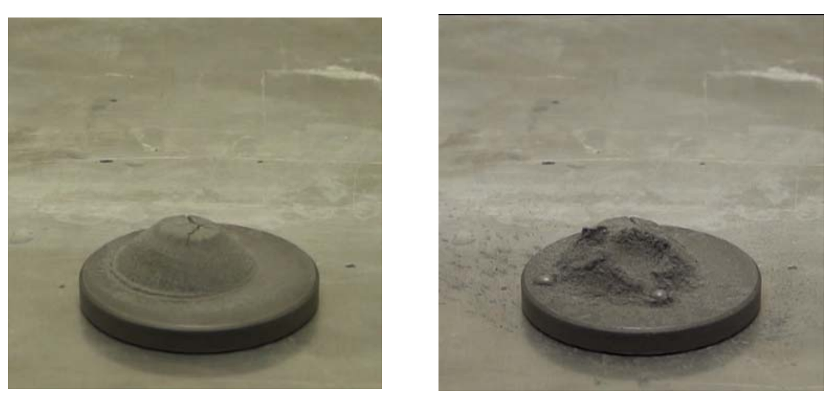
- **1) Calorimetry**

Argon gas flow with 30% RH at 40°C

Small exothermic reaction
products under analysis



- **2) UN test**
  - **Water drop**



t=0 s

No reaction with addition of H_2O drops

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Predictive Models

- Preliminary experiments suggest:
  - Exposure of media to humid environment leads to:
    - Exothermic reaction and H_2 generation
    - Low thermal conductivity of media causes temperature to rise
    - H_2 at surface and in pores burns if & when auto ignition temperature of 571°C is reached
    - Burning of H_2 initiates pyrolysis of media
- Correlations will be developed, in terms of non-dimensional parameters, that:
  - Predict whether H_2 ignition occurs
    - Predict time to ignition
  - Predict whether pyrolysis occurs
- Correlations will be developed on salient material properties of media and dimensions of media pile

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Task 2 Plans

- **Summarize results of calorimetric tests and UN tests in a DOE report for the $LiBH_4 + MgH_2$ material system**
- **Continue liquid phase and gas phase calorimetry of NH_3BH_3**
- **Identify amorphous reaction products (Raman, NMR)**
- **Assess risks based on observed thermo-chemical release**

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Task 3 Plan

- **Identify risk mitigation strategies including contaminants and poisons which will reduce exothermic releases.**
- Evaluate theoretical thermodynamics of mitigation strategies for water and air exposures initially on NH_3BH_3, $2LiBH_4+MgH_2$, $2LiH+Mg(NH_2)_2$, AlH_3 & $NaAlH_4$.
- Perform calorimetric experiments of mitigation strategies for water exposure at $0<T<50^oC$.
- Perform calorimetric experiments of mitigation strategies for conditioned air exposure at $0<T<100^oC$, $0<\%RH<100\%$.
- Identify reaction products.
- Assess mitigation strategies effectiveness based on observed thermo-chemical release.

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SRNL FYs ’07 & ‘08 Work

- Coordinate IPHE team to complete experimental analysis, compile results and disseminate findings and conclusions.
- Complete standardized tests UN hazards analysis tests on NH_3BH_3, $2LiH + Mg(NH_2)_2$ & AlH_3.
- Perform calorimetric experiments on environmental exposure reactions, assess reaction products and chemical kinetics as a function of T & %RH.
- Determine chemical reaction & thermal discharge rates to assess risks.